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SELECTION OF MEMBRANE MATERIALS BY LIQUID PHASE AFFINITY CHROMATOGRAPHY FOR NAPHTHA UPGRADING

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Selection of Membrane Materials by Liquid Phase Affinity Chromatography for Naphtha Upgrading

by

Colette Nader* and Brian Farnand**

SUMMARY

Preliminary work with liquid phase affinity chromatography has been used to select candidate materials for the reverse osmosis upgrading of naphtha. Emphasis has been upon the selectivity of the materials for the adsorption of high octane rating aromatic components with respect lower octane rating aliphatic components. Both aliphatic rich and aromatic rich conditions have been studied.

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Sélection des Matériaux Pouvant Servir à la Fabrication de Membrane par la Chromatographie Liquide d'Adsorption Dans le But d'Effectuer la Valorisation des Napthas par Osmose Inverse

par

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RESUME

La chromatographie liquide d'adsorption a été utilisée afin de sélectionner des matériaux pouvant servir à la fabrication de membrane dans le but d'effectuer la valorisation des naphthas par osmose inverse. Ces matériaux ont été étudiés en fonction de leur sélectivité vis-à-vis les composés aromatiques à indice d'octane élevé par opposition aux composés aliphatiques à faible indice d'octane. L'étude a été effectuée autant pour les concentrations élevées d'aromatiques que pour les concentrations élevées d'aliphatiques.

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INTRODUCTION

Membrane development for the upgrading of naphtha streams has been undertaken by CANMET/ERL, and this report is a preliminary statement of the results of this study.

Naphtha streams from synthetic crudes have poor octane ratings, usually based upon their low aromatic content (1). As well, refining of these streams is complicated by the presence of problematic compounds, usually containing nitrogen and sulphur or other heteroatoms. The primary goal of the membrane work is the improvement of the octane rating of naphtha by producing an aromatic rich stream and an aromatic lean stream. The latter would be available for catalytic upgrading. A secondary goal is the removal of nitrogen and sulphur containing components from the naphtha streams, also by using membranes.

Previous experience with the development of reverse osmosis in aqueous as well as non-aqueous solutions has demonstrated the utility of affinity chromatography for the qualitative and quantitative prediction of reverse osmosis and ultrafiltration performance (2,3,4,5). This work extends these principles, simplified by the use of pure solvents (toluene and heptane) as the carrier liquid to represent aromatic and aliphatic naphtha to the naphtha case. Because of this simplification, prediction of reverse osmosis performance cannot be made. However, speculation as to the nature of reverse osmosis performance can be inferred from these experiments.

The probes used in this work were chosen on the basis that they represent specific group contributions, extremes in size, or were found to be present in significant quantities in synthetic naphtha streams (6,7). The candidate membrane materials were: cellulose (CE); cellulose acetate E-398 (CA); cellulose acetate butyrate (CAB, 17% butyrated); cellulose triacetate (CTA); cellulose acetate hydrogen phthalate (CAHP); low density polyethylene (PE); and Teflon^{R}. With the exception of the latter two materials, reverse osmosis membrane fabrication details are available in the literature.

EXPERIMENTAL

A schematic diagram of the apparatus used for affinity chromatography is shown in Fig. 1. Single solute probe solutions of approximately 1% by weight of solute in carrier solvent were injected into the carrier stream and their retention times were reported. When the entire set of solutions was injected, the carrier solvent was changed. The new carrier solvent was passed through the

column to remove residual traces of the previous carrier. When a stable baseline for the refractive index detector was obtained, the second set of probes was injected.

The columns were filled with candidate membrane materials in powder form, usually in the 38-53 μm size range (sieved). In the cases of Teflon^R and PE powder, they were already supplied in a powder finer than the 38-53 μm size range. As well, because of the large amount of swelling of PE in toluene, "toluene pre-swollen" PE powder was used in the column. All of the columns were filled by dry powder methods.

The retention volume was determined for each probe, according to

$$V_R = t_R \cdot Q \qquad (1)$$

where V_R is the retention volume, t_R is the retention time, and Q is the carrier solvent's volumetric flow rate through the column. These are shown in Table 1 for the heptane carrier solvent case, and Table 2 for the toluene carrier case.

DISCUSSION

Because the candidate membrane materials' surface areas are unavailable and the solvent retention volumes were not determined, direct comparison between the data for the different materials in Tables 1 and 2 cannot be made. However, the relative ability to retain aromatic components can be compared. This can be quantified by calculating the ratios of retention volumes for various compounds and comparing these directly for the different candidate materials. These pairs were chosen on the basis of similar carbon atom content to minimize diffusion and steric exclusion effects. These are shown in Table 3 for the heptane carrier case and in Table 4 for the toluene carrier case.

On the basis of the information of Tables 3 and 4, the selection of materials for further study can be made. The CAB and CTA materials show the greatest selectivities for aromatics with respect to aliphatic compounds. Pyridine was also retained with respect to the aliphatic compounds for both materials, which may be taken as an indication of the preferential adsorption of polar compounds on these two materials. This shows promise for compounds with heteroatoms, since they are also considered to be polar in nature. Further, the values of the ratios of Tables 3 and 4 for common pairs indicate the preferential adsorption of aromatic components is more pronounced in heptane than in toluene. This is understandable as the toluene

carrier would compete with the aromatic probes for preferential adsorption. It is also an indication that the preferential adsorption of aromatic and polar components will be more pronounced in aliphatic rich naphthas.

CONCLUSIONS AND RECOMMENDATIONS

An indication of the different affinities of membrane materials for probe compounds chosen from naphtha components can be determined by affinity chromatography. Work of this nature should be continued with candidate membrane materials to determine their suitability for naphtha upgrading. Of the materials tested, cellulose triacetate and cellulose acetate butyrate demonstrate affinity for aromatic probes when compared with aliphatic probes. A test of their performance for the upgrading of naphtha should be made, since methods for reverse osmosis membrane fabrication with these two materials are available in the literature.

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TABLE 1

RETENTION VOLUMES FOR THE HEPTANE CARRIER CASE

	CE	CA	CTA	CAB	CAHP	PE	Teflon^R
Cycloheptane	1.34	1.60	2.68	2.60	1.70	2.61	1.04
Methylcycloheptane	1.39	1.56	2.68	2.57	1.78	2.70	1.10
Cyclohexane	1.36	1.56	2.60	2.60	1.52	2.76	1.12
Benzene	1.40	1.64	-	4.38	1.55	2.78	1.12
Toluene	1.36	1.64	-	3.73	1.57	2.73	1.12
p-Xylene	1.36	1.61	3.04	3.55	1.58	2.67	1.10
Ethylbenzene	1.34	1.58	3.09	3.56	1.52	2.64	1.10
Propylbenzene	1.36	1.56	3.06	3.38	1.81	2.70	1.10
Cumene	1.38	1.54	2.87	3.37	1.51	2.76	1.12
Mesitylene	1.42	1.57	2.85	3.35	1.59	2.70	1.05
Butylbenzene	1.34	1.58	2.82	3.18	1.51	2.64	1.03
Naphthalene	1.40	1.66	2.69	6.48	1.56	2.78	1.16
Methylnaphthalene	1.38	1.60	3.33	5.85	1.51	2.73	1.09
bis-Phenol	1.36	1.65	4.41	7.03	1.67	2.76	1.05
di-Butylbenzene	1.43	1.56	2.58	2.69	1.62	2.67	1.04
2,2-Dimethylbutane	1.32	1.58	2.68	-	-	2.73	-
Hexane	1.38	1.73	-	-	1.69	2.76	1.19
Heptane	-	-	-	-	-	-	-
i-Octane	1.35	1.81	-	2.56	1.79	2.32	1.13
Hexadecane	1.36	1.54	2.52	2.27	1.46	2.47	0.99
Tetratetracontane (C44)	1.31	1.53	-	2.15	1.39	-	-
1-Hexene	1.35	1.83	-	-	-	2.75	1.08
1-Nonene	1.35	1.58	2.60	2.50	1.51	2.64	1.09
Pyridine	1.48	1.81	npk	npk	npk	2.78	1.28
Toluenethiol	-		-	-	-	2.67	1.08
Material Weight, g	0.586	0.688	0.622	1.250	0.913	0.382	0.471
Average Flowate, mL/min.	0.267	0.288	0.271	0.294	0.222	0.273	0.270

npk = peak was not eluted or visible, equivalent to a large value.

TABLE 2

RETENTION VOLUMES FOR THE TOLUENE CARRIER CASE

	CE	CA	CTA	CAB	CAHP	PE	Teflon^R
Cycloheptane	1.47	1.59	3.30	2.14	1.74	2.74	1.20
Methylcycloheptane	1.49	1.63	2.89	2.68	1.62	2.71	1.19
Cyclohexane	1.43	1.64	3.21	2.16	-	2.71	1.24
Benzene	1.51	1.97	-	-	1.81	2.74	1.14
Toluene	-	-	-	-	-	-	-
p-Xylene	1.49	1.90	3.74	3.27	1.73	2.71	-
Ethylbenzene	1.52	1.90	-	-	1.83	-	1.16
Propylbenzene	1.52	1.85	3.36	2.41	1.81	2.68	1.14
Cumene	1.49	1.90	-	2.16	1.78	2.71	-
Mesitylene	1.52	1.84	-	-	1.83	2.74	-
Butylbenzene	1.49	1.89	3.64	2.55	1.77	2.71	-
Naphthalene	1.47	1.75	3.02	3.06	1.87	2.62	-
Methylnaphthalene	1.49	1.74	3.06	2.35	1.84	2.59	1.11
bis-Phenol	1.49	1.67	2.78	2.32	1.83	2.56	1.13
di-Butylbenzene	1.52	1.86	-	1.98	1.93	2.74	1.26
2,2-Dimethylbutane	1.49	1.67	3.73	2.19	1.81	2.65	1.18
Hexane	1.49	1.72	3.15	-	1.74	2.80	1.15
Heptane	1.44	1.64	3.15	2.11	1.78	2.68	-
i-Octane	1.47	1.63	3.04	2.09	1.71	2.59	-
Hexadecane	1.49	1.67	3.06	2.35	1.42	2.59	1.15
Tetratetracontane (C44)	1.49	1.88	-	-	1.80	-	-
1-Hexene	1.49	1.74	3.34	2.74	1.78	2.74	-
1-Nonene	1.49	1.67	3.06	2.05	1.75	2.71	-
Pyridine	1.49	1.90	3.67	npk	1.77	2.77	1.27
Toluenethiol	-	-	-	-	-	2.56	1.12
Material Weight, g	0.586	0.688	0.662	1.250	0.913	0.382	0.471
Average Flowate, mL/min.	0.293	0.322	0.306	0.297	0.297	0.188	0.293

npk = peak was not eluted or visible, equivalent to a large value.

TABLE 3

RATIOS OF RETENTION VOLUMES WITH HEPTANE AS THE CARRIER SOLVENT

Solute A/Solute B	$V_{R,A}/V_{R,B}$						
	CE	CA	CTA	CAB	CAHP	PE	Teflon[R]
toluene/i-octane	1.01	0.91	-	1.46	0.88	1.17	0.99
benzene/hexane	1.01	0.95	-	-	0.92	1.01	0.94
ethylbenzene/i-octane	1.00	1.05	-	1.57	0.85	1.14	1.11
toluene/methylcyclohexane	1.01	1.05	-	1.45	0.88	1.01	1.02
benzene/cyclohexane	1.02	1.05	-	1.68	1.02	1.01	1.00
bisphenol/hexadecane	1.00	1.07	1.75	3.10	1.14	1.12	1.06
propylbenzene/1-nonene	1.01	0.99	1.17	1.35	1.20	1.02	1.01
pyridine/2,2-dimethylbutane	1.12	1.14	-	-	-	1.02	-
Average, Aromatic/Aliphatic	1.01	1.01	-	1.85	0.95	1.08	1.02

[a] No peak for pyridine was eluted, which implies a large value for $(V_{R,A}/V_{R,B})$.

[b] The inverse of 0.85 is 1.18. This can also be used to compare with the other values in this table.

TABLE 4

RATIOS OF RETENTION VOLUMES WITH TOLUENE AS THE CARRIER SOLVENT

Solute A/Solute B	$V_{R,A}/V_{R,B}$						
	CE	CA	CTA	CAB	CAHP	PE	Teflon[R]
benzene/hexane	1.01	1.15	-	-	1.04	0.98	0.99
ethylbenzene/i-octane	1.03	1.17	-	-	1.07	-	-
benzene/cyclohexane	1.06	1.20	-	-	-	1.01	0.92
bisphenol/hexadecane	1.00	1.00	0.91	0.99	1.29	0.99	0.98
p-xylene/heptane	1.00	1.16	1.18	1.55	0.97	1.01	-
propylbenzene/1-nonene	1.02	1.14	1.10	1.18	1.03	0.99	-
pyridine/2,2-dimethylbutane	1.00	1.14	0.98	-	0.98	1.04	1.08
Average, Aromatic/Aliphatic	1.02	1.14	1.05	1.27	1.09	1.00	0.96

[a] No peak for pyridine was eluted, which implies a large value of $V_{R,A}/V_{R,B}$.

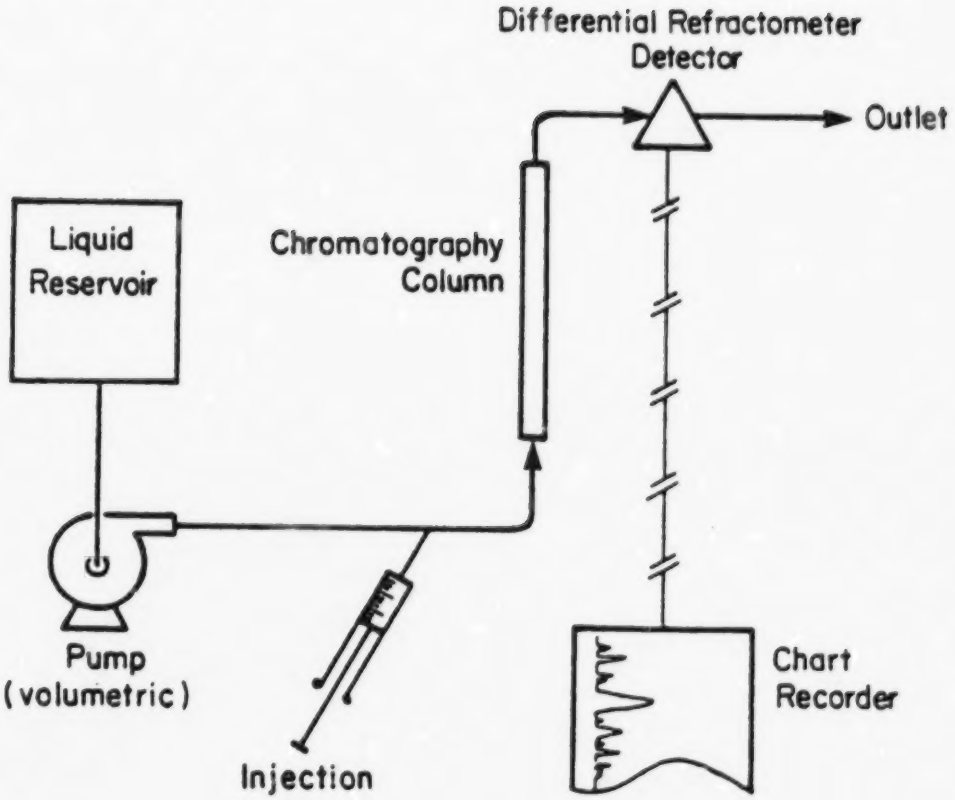

Figure 1 Schematic Diagram of Liquid Chromatographic Apparatus

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